26p.

UNIVERSITY OF WISCONSIN

THEORETICAL CHEMISTRY INSTITUTE

TYPE OF REPORT: SEMI-ANNUAL REPORT to National
                                Aeronautics and Space
                                Administration

NUMBER OF REPORT: Two (2)

PERIOD REPORT COVERS: 1 January 1963 through 30 June 1963

GRANT NUMBER: NsG-275-62

DATE: 30 June 1963

SIGNATURES:

Joseph O. Hirschfelder
Principal Investigator

C. F. Curtiss
Principal Investigator

NASA SEMI-ANNUAL PROGRESS REPORT

On July 1, 1962 we received our first NASA grant, and our Theoretical Chemistry Institute came into existence. Our avowed purpose is to reduce molecular quantum mechanics to practice. Then to use the quantum mechanics as input information in the statistical mechanical formulation leading to the calculation of the chemical and physical properties of materials and the chemistry of the upper atmosphere. Prior to July 1962 our group was capable and had an excellent research background in statistical mechanics, the kinetic theory of gases, and the theory of flames and detonations. For example, our research on the heat transfer in dissociating gases has proven to be very useful in connection with the re-entry problem. However, in recent years we had not done much research in molecular quantum mechanics. Thus, last summer we were faced with two major problems: (1) building up a staff, and (2) developing a suitable research program. We believe that we have been successful on both scores.

STAFFING

1. Saul T. Epstein, full Professor jointly with the Department of Physics and the Theoretical Chemistry Institute. Epstein is a very brilliant theoretical physicist trained at M.I.T., consultant at Brookhaven, and formerly professor at the University of Nebraska. His interests are very broad and include the set of fundamental problems which confront us in theoretical chemistry. He is extremely useful to us because he can show us how to apply to our problems the scattering techniques and other new developments in nuclear and solid state physics, as well as field theory. As a member of our group, he helps to solidify our contacts with the Physics Department and the theoretical physicists at Wisconsin.

2. Richard B. Bernstein, full Professor jointly with the Department of Chemistry and the Theoretical Chemistry Institute. Bernstein is one of the foremost experts in both experimental and theoretical aspects of low-energy molecular beams. Much of his work finds immediate applications in the interpretation of the properties of the upper atmosphere of the earth and of the planets. This work is also valuable in providing a solid foundation for the theory of chemical kinetics.

3. W. Byers Brown, Associate Professor jointly with the Department of Chemistry and the Theoretical Chemistry Institute. Byers Brown was trained in Manchester and subsequently taught at the University of Edinburgh. He is an expert both in molecular quantum mechanics and the kinetic theory of gases. He has a wide knowledge of most phases of mathematics and of science--extraordinary breadth. As an officer in the research branch of the British Air Force, he learned a great deal about problems in aerodynamics, meteorology and the upper atmosphere. This summer he is working with an Argonne National Laboratory group at ARCO on the equations of state problems which arise in high temperature nuclear reactors. Byers Brown is directing a number of graduate students at the Theoretical Chemistry Institute on an assortment of molecular quantum mechanics and equation of state problems. Although he is quite young, I believe that he is a scientist of great promise.

4. Michael B. McElroy has been offered a post as Assistant Professor jointly with the Department of Astronomy and the Theoretical Chemistry Institute. He may spend the year 1963-64 at Mount Kitts National Astronomical Observatory and return to Wisconsin next summer. McElroy is a former student of Dalgarno and Bates at Belfast. He is currently working on molecular scattering problems, which are directly applicable to an understanding of the upper atmosphere. On April 17, 1963, he gave a talk (together with Dalgarno) at the American Geophysical Union--NASA Conference in Washington. In his talk, which was entitled "Fluorescence of Solar Ionizing Radiation," he presented evidence that the electron temperatures in the upper atmosphere are much greater than had previously been supposed.

5. Daniel D. Konowalow, Assistant Director, Theoretical Chemistry Institute, received his Ph.D. at the University of Wisconsin and subsequently worked at the du Pont Polychemical Department.

6. Dr. Stuart E. Lovell, Assistant Professor jointly with the Department of Numerical Analysis and the Theoretical Chemistry Institute. Lovell received his Ph.D. in physical chemistry at Brown University under Dr. Cole. His research has been in the field of solution chemistry, properties of high polymers, and numerical analysis. Lovell is valuable to us in helping us to apply the best techniques of high speed computing machine

coding to our problems. He also forms a link between our group and the Numerical Analysis Department.

You can see from the above paragraphs that we have received excellent cooperation from many of the departments of the University and from the University Administration. Thus, our group is directly interdisciplinary and will become more so during the coming years. We have expecially strong ties with the Departments of Chemical and Mechanical Engineering. Indeed, we expect that in the next two or three years as our work becomes more practical these ties will become closer. I personally want to brag that the American Society of Mechanical Engineers has elected me to become an honorary member at a banquet to be held in Philadelphia next November. Also, I have been appointed a charter member of the Board of Directors of the American Institute of Engineering Science. We do not anticipate any large expansion of personnel in the future. We believe that our present group has the technical capacity to tackle effectively the types of problems with which we are concerned.

During the next year we will have three visiting professors: Boris Musulin, Associate Professor of Chemistry from Southern Illinois University; Professor Thomas H. Walnut, Associate Professor of Chemistry from Syracuse University and John S. Dahler, Professor of Chemical Engineering from the University of Minnesota. Musulin and Walnut are coming for the whole year, Dahler for the spring semester. We will pay for a portion of Musulin's salary. Dahler and Walnut will be coming at no cost to our institute. The fact that we are attracting professors to come for their sabbatical leaves is an indication that our institute is successful.

At the present time we occupy a small amount of space in unit one of the Chemistry Research Laboratory together with an old frame house across the street from unit one. Next September we will be crowded. Within another year our "space" problem will be acute. Thus, we very much welcome the NASA grant ▮▮▮▮▮▮▮ to provide us with additional space in the second unit of the chemistry building which should be completed in 1966. According to present plans, this grant will provide us with a complete floor of the second unit. The State Building Commission has approved the preliminary plans and purchased the necessary land. It is expected that within the next few weeks an architect will

be hired to prepare detailed drawings. We expect to occupy the new quarters in 1966.

We are planning to use that portion of our initial research grant earmarked for a computer to purchase a multi-purpose configuration. Our computer will act as an independent unit and also as a satellite and remote-control link to the University Numerical Analysis Laboratory main computer (which currently is a CDC 1604). Such flexibility is necessary to handle efficiently the large and varied computational programs we are now generating. We expect to use our computer for running small problems as well as debugging larger problems which will be run on the University's large central processor. Such a system should give us the largest return for our computational dollar. At the present the University's CDC 1604 is adequate to handle the bulk of our computing needs. This fact and the rapid changes in remote-control and computer capabilities mitigates against making a purchase until the last possible moment. According to our best estimates we should have our computer installed when we occupy our enlarged quarters in 1966. About this same time we anticipate that the University will replace the CDC 1604 by a considerably larger computer.

RESEARCH

Our principal question regarding research last year was "How can we best calculate intermolecular forces and potential energy surfaces?" In order to answer this question we sought the advice of the greatest experts in the world, and we made an extensive survey of the literature. During the course of this last year, we have had a great many visitors, who, together with the topics of their lectures to our group, are listed in the Appendix. Then too, I was most fortunate in working with Löwdin and his group at the University of Florida during the months of January and February. Gradually it became evident to us that the great advances in molecular quantum mechanics would not come in from the Rayleigh-Ritz variational method which for thirty years has dominated the quantum mechanics of stationary states. Rather, it appears that the great advances will come from perturbation theory. In 1956, Dalgarno showed that it is feasible to solve the perturbation equations explicitly without recourse to expansions in terms of a spectral distribution of a complete

set of solutions to the unperturbed problem. With this perturbation theory, Dalgarno has started to make excellent calculations of long-range intermolecular forces. On the other hand, Sinanoğlu has shown that in chemical problems involving a single bond structure the Hartree-Fock or extended Hartree-Fock solutions take care of most of the long-range interaction between electrons. Thus, the difference between the exact solution and the Hartree-Fock solutions can be treated as a perturbation problem with the use of Brueckner-type many body techniques. This divides the molecular problem up into a set of two electron problems, each of which appears to be tractable with the use of perturbation theory. Thus, in the solution of a molecular quantum mechanics problem, perturbation would be applied at three stages. First in approximating the Hartree-Fock solutions; second in breaking up the residual correlation problem into a series of two electron problems; and third in the solution of two electron problems. Currently, we are developing new and improved techniques for solving the perturbation equations. For example, in our report TCI-21 (to be published in the ~~Proceedings of the National Academy of Sciences~~ *Journal of Chemical Physics*) I have developed an iterative scheme of starting with a trial wave function, calculating the wave function through the first order in almost the usual fashion, then using this wave function through the first order as a new trial function in a new perturbation problem. This procedure converges extremely rapidly. For example, after the sixth iteration the energy is accurate up to the 128th power of a perturbation parameter! Also, I have found a simple and accurate method for treating degenerate or almost degenerate energy levels. Currently, we are applying these techniques to a graduated family of examples starting with the helium atom and with H_2^+.

During the past academic year, we have been fortunate to have the help and advice of Professor Egil A. Hylleraas, Professor of Theoretical Physics, University of Oslo. Hylleraas is one of the grand old men of quantum mechanics and the inventor of most of the techniques which we use in molecular quantum mechanics. Hylleraas' most important achievement during the course of this year has been the development of a new method for solving the inverse scattering problem. That is, given the phase shifts for a central field potential scattering problem, determine the size and shape of the potential well. The Hylleraas method is much

simpler and easier to use than the Gell-Mann and Levitan technique which it
supersedes. This will be a boon to both the nuclear physicists and to our
molecular beam scattering workers.

Professor C. F. Curtiss has been greatly concerned with the quantum
mechanical corrections to the transport properties of gases at extremely
low temperatures. This involves the WBK calculation of phase shifts from
effective potentials (the radial potential plus the centrifugal potential)
involving three classical turning points. Previous treatments of this
problem have been erroneous. Curtiss has solved this problem correctly
with the use of a very novel type of expansion of integrals involving
Bessel functions of large argument and large order. Curtiss' expansion is
very interesting to the applied mathematicians, since the same techniques
may be applied to the asymptotic expansion of a variety of transcendental
functions. Currently Curtiss is applying his methods to a three body
scattering problem.

The remainder of the Theoretical Chemistry Institute research during
the last year is summarized in the Appendix.

At the present time, we are planning an international symposium on
molecular quantum mechanics to be held at the University of Wisconsin
July 12-16, 1965. Originally we had expected to hold this symposium in
the summer of 1964, however, this date was changed to avoid a conflict
with a Gordon Conference on the same topic. We have received excellent
cooperation from our scientific associates throughout the world. We have
received support from the University of Wisconsin Administration and many
of the different University departments. The Chemistry Department has
been especially helpful. We have received a great deal of help from the
Army Applied Mathematics Center and expect that during the course of the
next year, with Barkley Rosser becoming the new director, our association
with them will become stronger. We are tremendously happy that NASA has
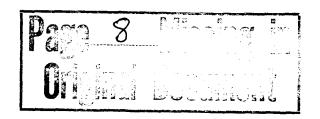given us this opportunity to make a major contribution to the space effort.

Upon receiving our NASA grant last summer, the A.E.C. and U. S. Army
Research Office (Durham) terminated their research contracts with us, and
the Naval Bureau of Weapons reduced their research support.
Our Air Force contract is terminating September 15, 1963. This
leaves us with only NASA financial support. However, I was informed last

funds

week that the N.I.H. expects to give us ████ to be spent during a three year period for health related research. We intend to use these N.I.H. funds to calculate the forces between large aggregates. This would be a good adjunct to our calculations of intermolecular forces. However, the forces between aggregates require the combined techniques of colloid chemistry, molecular quantum mechanics, field theory, and solid state physics. The colloid aspects are probably the most important. Theoretical colloid chemistry in the United States is becoming a forgotten art, with only Peter Debye to maintain the traditions. Therefore, we are seeking help from our scientific friends in Holland where colloid chemistry is flourishing.

We are glad to have the N.I.H. support, as it helps to give financial stability to our group. However, we very much hope that NASA will continue to furnish our primary support.

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Theoretical Chemistry Institute Visitors during Fiscal Year 1962-63

NAME AND ADDRESS	PERIOD OF VISIT	LECTURES GIVEN
Professor Werner Ringel Max-Planck Institut für Physik und Astrophysik Institut für Astrophysik Munich 23, Germany	7/1/62 to 8/31/62	
Mr. S. Cavalas Leszcinski Department of Chemistry University of Florida Gainesville, Florida	6/18/62 to 8/31/62 and 5/1/63 to 7/31/63	

Dr. John A. Pople
National Physical Laboratory
Teddington, Middlesex
England
	10/15/62 to 10/25/62	Electronic Structure of Small Molecules
		Electronic Excited States
		Diamagnetism and Nuclear Magnetic
		  Resonance
		Paramagnetism and Electron Spin
		  Resonance
		Theory of Melting of Molecular Crystals
		Lattice Vibrations in Molecular Crystals

Professor Leland Allen
Department of Chemistry
Princeton University
Princeton, New Jersey
	11/5/62 to 11/9/62	Electron Correlation in Atoms and
		  Molecules
		Spin Correlated Orbitals and Semi-
		  empirical Electronic Structure Theory
		Improvement in the Resolution and
		  Sensitivity of Instruments Appropriate
		  to Chemistry and Biochemistry

Professor Saul Epstein Department of Physics University of Nebraska Lincoln, Nebraska	10/1/62 to 10/4/62 and 6/10/63 to 6/26/63	Mach's Principles Density Matrices
Professor John Dahler Dept. of Chemical Engineering University of Minnesota Minneapolis, Minnesota	11/4/62 to 11/16/62	
Professor Oktay Sinanoglu Department of Chemistry Yale University New Haven, Connecticut	11/12/62 to 11/14/62	Many Electron Theory of Atoms, Molecules and Their Interactions
Professor A. Dalgarno Dept. of Applied Mathematics The Queen's University of Belfast Belfast, North Ireland	11/5/62 to 11/13/62	Thermal Scattering by Diatomic Molecules Oscillator Strengths and Sum Rules Perturbation Theory for Atomic Systems

NAME AND ADDRESS	PERIOD OF VISIT	LECTURES GIVEN
Professor Richard Bernstein Department of Chemistry University of Michigan Ann Arbor, Michigan	12/11/62 to 12/12/62	
Dr. James C. Browne Department of Physics University of Texas Austin, Texas	2/13/63 to 2/15/63	The University of Texas Molecular Physics Program
Professor John Ross Department of Chemistry Brown University Providence 12, Rhode Island	4/1/63 to 4/2/63	Theory of Molecular Beam Scattering
Dr. Yngve Öhrn Quantum Chemistry Group Rundelsgrand 2A Department of Chemistry Uppsala, Sweden	4/1/63 to 4/30/63	Symmetry in Hartree-Fock Calculations Wave functions Incorporating Inter- electronic Coordinates
Dr. Robert K. Nesbet Research Laboratory International Business Machines Corporation Monterey and Cottle Roads San Jose 14, California	4/29/63 to 5/3/63	Electronic Correlation, the Hartree-Fock Theory, and the Physical Properties of Molecules
Dr. Lionel Salem Department of Chemistry Harvard University Cambridge 38, Massachusetts	5/1/63 to 5/21/63	Hellmann-Feynman Theorem (with particular emphasis on reliability, repulsive forces, force constants, and inter- action constants)
Professor John R. Platt Department of Physics University of Chicago Chicago 37, Illinois	5/6/63 to 5/7/63	A "Book Model" of Genetic Information Transfer in Cells and Tissues
Professor I. Prigogine Universite Libre de Bruxelles Avenue F-D, Roosevelt 50 Bruxelles, Belgique	5/24/63	The Present State of Nonequilibrium Statistical Mechanics
Dr. Robert Sack Department of Mathematics Royal College of Advanced Technology Salford 5, Lancashire England	5/1/63 to 8/16/63	A Basic Approach to Perturbation Theory

NAME AND ADDRESS	PERIOD OF VISIT	LECTURES GIVEN
Professor Charles Beckel Department of Physics Georgetown University Washington 7, D. C.	6/17/63 to 6/21/63	Vibrations of Diatomic Molecules Relating Vibrational Characteristics to Electronic Properties of Diatomic Molecules Application of the Second-Order WBK Approximation to Radial Problems
Professor Sergio Carra Institudo de Chimica Fisica Universita Degli Studi fi Milano Via C. Saldini, 50, Milano, Italy	5/63 to 11/63	
Professor John S. Rowlinson Dept. of Chemical Engineering and Chemical Technology Imperial College University of London South Kensington London S.W. 7., England	6/16/63 to approx. 9/63	Some Recent Advances in the Theory of the Equilibrium Properties of Fluids

UNIVERSITY OF WISCONSIN THEORETICAL CHEMISTRY INSTITUTE STAFF LIST

FISCAL YEAR 1962-63

NAMES	TITLES

Professors

Joseph O. Hirschfelder	Professor - permanent
Charles F. Curtiss	Professor - permanent
Frank C. Andrews	Assistant Professor - permanent
Egil A. Hylleraas Physics Institute University of Oslo Blindern, Norway	Visiting Professor - academic year
Prof. J. D. Porter Department of Chemistry Union College Schenectady 8, New York	here on sabbatical leave - academic year

Post-doctorates

Daniel D. Konowalow	Assistant Director - permanent
Marinus J. Offerhaus Instituut voor Theoretische Fysica Universiteit van Amsterdam Roeterstraat 1A Amsterdam-C, Nederlands	Wisconsin Alumni Research Foundation Fellow and Project Associate from 9/61 to 8/62
Peter D. Robinson Mathematics Institute Oxford University Oxford, England	Project Associate from 9/61 to 9/62
William Byers Brown Department of Chemistry University of Edinburgh West Mains Road Edinburgh 9, Scotland	Project Associate/Lecturer (Associate Professor beginning 9/63)
Michael B. McElroy Department of Applied Mathematics Queen's University Belfast, North Ireland	Project Associate from 9/62 to present
Sidney Gordon	N.S.F. post-doctorate fellow and Project Associate from 2/62 to 5/63
Robert Hermann	N.S.F. post-doctorate fellow from 2/62 to 1/63

Computing Staff

Stuart E. Lovell - Ph.D. in Chemistry; Project Associate (Assistant Professor
jointly with U.W. Numerical Analysis Dept. beg. 7/63)

Marion H. Taylor - B.S. in Mathematics; Project Supervisor - permanent

NAMES   TITLES

Computing Staff - continued

Carol B. Monash - B.S. in Mathematics; Project Assistant - permanent

Sharon R. Albright - B.S. in Mathematics; Project Assistant - through 4/63

Graduate Students

Raymond J. Beshinske	Research Assistant
Tai Yup Chang	Research Assistant
Earl F. Epstein	Teaching Assistant - Chemistry Dept.
Michael M. Feen	Research Assistant
Jerome B. Heath	Research Assistant
David K. Hoffman	Research Assistant
John H. Huntington	Research Assistant
R. Soesanto Imam-Rahajoe	Agency for International Development Scholarship
Sungwoon Kim	Research Assistant
Donald Kouri	Research Assistant
Bowen Liu	Research Assistant
William D. Lyon	Research Assistant
Robert L. Matcha	Research Assistant
William J. Meath	Research Assistant
John Mueller	N.S.F. Fellow
George V. Nazaroff	Research Assistant
Russell T. Pack	N.S.F. Fellow
Theodore Provder	Research Assistant
Kenneth M. Sando	Research Assistant
Herbert T. Wood	Research Assistant

Office Staff

Karen A. Rick - B.S. in Economics	Project Assistant
Gloria M. Franz	Stenographer II

Phyllis L. Hergenrader (husband working for Ph.D. in Zoology)
                                    Typist III ending 6/63

Frieda Dianna Luthy (husband working for B.S. in Commerce)
                                    Clerical Assistant from 9/62 to 6/63

Barbara R. Lien (Senior in Elementary Education)
                                    Clerical Assistant/p.t. student help
                                    from 7/62 to 1/63

NAMES	TITLES

Office Staff - continued

Judith M. Williams (husband working for Ph.D. in Chemical Engineering)
Clerical Assistant summer 1962

Catherine E. Crowley — Typist III beginning 5/63

Gladys M. Kraberni (Sophomore majoring in Foreign Languages)
Clerical Assistant beginning 6/63

Robert R. Gersbach (Senior in Chemistry) Part-time student help through 1/63

Mark J. Van Duser (Junior in Electrical Engineering)
Part-time student help 9/62 - 6/63

Margaret F. Magner (working for M.S. in English)
Part-time student help 1/63 - 6/63

Gerhardt P. Schroeder (Senior in Mechanical Engineering)
Part-time student help beginning 6/63

Miscellaneous

Frederick D. Mackie (Senior in Physics) Undergrad Project Assistant 6/62 to 9/62

Dennis W. Kuba (Senior in Math/Physics) Undergrad Project Assistant 10/62 to 5/63

APPENDIX - continued

Summary of Research at the University of Wisconsin Theoretical Chemistry
Institute during Fiscal Year 1962-63

"The Effects of Degeneracy on the Inelastic Scattering of Electrons and
Protons by Hydrogen Atoms" by P. D. Robinson   dated 2 July 1962
(supported by Air Force) - Report No. WIS-AF-22.

Abstract

An investigation is made of the effects of $2s{:}2p$ degeneracy on cross-
sections for the $1s \longrightarrow 2p$ and $1s \longrightarrow 2s$ excitation of hydrogen atoms by electron
and proton impact. The initial relative energy ranges considered are 10.2 to
50 e.v. for electrons and 0.25 to 50 k.e.v. for protons. A simple rotating
axis approximation of Bates is employed, and the degeneracy is allowed for by
using "spheroidal" atomic wave functions in the matrix elements rather than
pure 2s or 2p functions. These spheroidal functions are varying linear combina-
tions of 2s and 2p, and are the correct zero-order functions for the atom per-
turbed by a charge particle. The degeneracy effects are measured by comparing
the "direct" cross-sections found using the pure 2s and 2p functions with the
"indirect" cross-sections obtained from the spheroidal functions. The in-
direct results are quite different from the direct ones for slow collisions,
both for electron and for proton impact. Comparisons are made with the Born
Approximation, with certain more refined results of other authors, and (for
electron impact) with the experimental evidence. The indications are that
the indirect cross-sections are the better for slow collisions, and it is
concluded that allowance should certainly be made for degeneracy effects if
accurate excitation cross-sections are desired.

"Natural Expansion of Exact Wave Functions II. The Hydrogen Molecule Ground State"
by Ernest R. Davidson and Leon L. Jones   dated 3 July 1962
(supported by Bureau of Naval Weapons) - Report No. CM-1024.
Published in J. Chem. Phys. 37, 12, 2966 (December 1962).

Abstract

The Kolos and Roothaan wave function for H_2 has been analyzed into
natural orbitals. It was found that the first natural orbital is nearly the
SCF function. The first four natural orbitals provide a good description of
the molecule and give a total energy of -1.169884 Hartrees. Beyond the first
four terms, the natural expansion becomes more slowly convergent.

"The Virial Theorem and Its Generalization in Scattering Theory" by Peter D. Robinson and Joseph O. Hirschfelder   dated 13 August 1962
(supported by NASA) - Report No. WIS-TCI-1.
Published in Phys. Rev. 129, 3, 1391 (February 1963).

Abstract

Heretofore the hypervirial theorems recently introduced by Hirschfelder have only been applied to bound state systems. In this paper it is shown that, with certain modifications, these theorems can also be applied to free systems, and, in particular, to scattering problems. The new form of the general hypervirial theorem is derived, and the theory is illustrated with the problem of a particle scattered by a central field. The ordinary virial theorem is deduced, together with other results of physical interest. Both classical and quantum-mechanical formalisms are considered, and in some cases the semi-classical approximation links corresponding results.

"On Sound Propagation in a Monatomic Gas" by M. J. Offerhaus
(supported by NSF) - Report No. WIS-NSF-20.   dated 29 August 1962

Abstract

Two methods for a theoretical discussion of sound propagation in a monatomic gas are discussed; they both aim at finding periodic solutions, one of the hydrodynamical equations, the other of the Boltzmann equation, and we refer to them as the hydrodynamical and the kinetic method. Both lead to solutions on successive levels of approximation, the first by gradually including, in the hydrodynamical equations, terms with gradients of higher order, the second by gradually increasing the number of functions from which to build a velocity distribution.

The main result reached by either method is a law of attenuation (dispersion and absorption) of the sound; the forms which this law takes, in both treatments, in consecutive approximations, are discussed and compared.

The treatment given holds for a gas with a Maxwellian intermolecular potential but the results can, in good approximation, be taken over to a real monatomic gas.

A comparison is finally made with experiments in monatomic gases done by Greenspan, who has extended his measurements into the region where the sound frequency becomes comparable to the collision frequency by decreasing the latter. It is shown that in this region the available approximation schemes prove necessarily inadequate.

"Comment on the Use of United-Atom Expansions" by Werner A. Bingel
(supported by NASA) - Report No. WIS-TCI-3.   dated 8 August 1962
Published in J. Chem. Phys. $\underline{38}$, 1, 274 (January 1963).

"Hyperviral Theorems for Variational Wave Functions in Scattering Theory"
by Saul T. Epstein and Peter D. Robinson   dated 7 September 1962
(supported by NASA) - Report No. WIS-TCI-2.
Published in Phys. Rev. $\underline{129}$, 3, 1396 (February 1963).

Abstract

The form of hypervirial theorem which is appropriate in scattering
theory is discussed in general terms. It is shown that variational wave
functions which are optimized in accordance with Kohn's variational principle
do satisfy hypervirial theorems. Thus such theorems may be useful in
selecting approximate wave functions to give accurate phase shifts or scattering
amplitudes. The situation is analogous to that of energy-optimized wave functions
for bound state systems.

"Transport Properties of Rigid Asymmetric Top Molecules" by Michael M. Feen
(supported by NSF) - Report No. WIS-NSF-21.   dated 21 September 1962

Abstract

In previous papers, an expression was derived for the coefficient of shear
viscosity of a gas made up of rigid ovaloids, in terms of an integral over the
surfaces of the two colliding molecules. The evaluation of this integral for
a model in which the molecule does not possess an axis of symmetry is discussed.

"Non-Uniform Scaling of an Approximate H_2^+ Wave Function" by William J. Meath
and Joseph O. Hirschfelder   dated 29 October 1962
(supported by Air Force) - Report No. WIS-TCI-4.
Accepted for publication in J. Chem. Phys.

Abstract

The approximate wave function considered for the H_2^+ molecule is

$$\psi = N \left[\begin{array}{c} \exp\left\{-s\left[\gamma^2(x^2+y^2) + (z+R/2)^2\right]^{\frac{1}{2}}\right\} \\ +\exp\left\{-s\left[\gamma^2(x^2+y^2) + (z-R/2)^2\right]^{\frac{1}{2}}\right\} \end{array} \right] .$$

Energy optimization of the non-uniform scaling parameter, γ, results in
the satisfaction of the "one-coordinate" virial theorem

$$-(\hbar^2/2m)\int \psi(\partial^2/\partial x^2)\psi d\tau = (\tfrac{1}{2})\int \psi x(\partial V/\partial x)\psi d\tau .$$

Similarly the energy optimization of the uniform scaling parameter, s,
results in the satisfaction of the usual virial theorem. The simultaneous
application of these two types of scaling is also discussed.

"Quantum Mechanical Solutions Obtained by Truncated Reaction Operators" by William J. Meath, S. Osvaldo Goscinski, Kenneth M. Sando, and Joseph O. Hirschfelder   dated 21 November 1962
(supported by NASA, Air Force, and Bureau of Naval Weapons)-Rpt. No. WIS-TCI-5.

Abstract

The use of truncated basis sets, comprised of eigenfunctions of the unperturbed Hamiltonian H_o , is discussed as a practical method for obtaining (i) an approximate solution for the reaction operator equation, $E_q = E_q^{(o)} + \langle \varphi_q | t | \varphi_q \rangle$; (ii) an approximate wave function for the perturbed system. The solution employs an iterative method which yields the matrix elements of the reaction operator. Connections between this approximate solution of the reaction operator equation and the linear variational, the Brillouin-Wigner and the Feenberg methods are derived.

"Kinetic Theory of Non-spherical Molecules V." by C. F. Curtiss and J. S. Dahler (supported by NASA and NSF) - Rpt. No. WIS-TCI-6.   dated 19 November 1962
Published in J. Chem. Phys. <u>38</u>, 10, 2352 (May 1963).

Abstract

A generalized Boltzmann equation for fluids composed of molecules with arbitrary internal degrees of freedom and which interact according to classical mechanics through arbitrary, non-central, pair-additive forces is developed using techniques similar to those used by Hollinger and Curtiss. Several special cases are considered: 1). molecules which interact only through impulsive forces of repulsion, 2). molecules for which the only internal degrees of freedom are rotational degrees, and 3). a combination of both special cases. The third special case leads to a Boltzmann equation appropriate to a fluid composed of rigid non-spherical molecules, and provides a firm basis upon which to develop a formal kinetic theory. As a special example we consider a gas made up of rigid, convex, non-spherical molecules with symmetric top mass distributions. Rigorous equations of hydrodynamics are presented for such a fluid. It is shown that the kinetic theory of a dilute multicomponent system of these molecules is formally the same as that for the loaded sphere system recently studied by Dahler and Sather. Finally, it is shown how the methods developed by these authors can be applied to the problems of solving the Boltzmann equation and of calculating the transport coefficients for the non-spherical molecular species considered in the present paper.

"Solutions for Complex Systems of Chemical Reaction Kinetics: II. An Irreversible Unimolecular Reaction Followed by a Reversible Unimolecular Reaction" by Dennis W. Kuba and Daniel D. Konowalow   dated December 1962 (supported by Air Force) - Report No. ARL 63-44.

Abstract

This is the third of a series of reports, in each of which a hypothetical reaction system with an idealized type of chemical kinetics is carefully scrutinized. The analytical solutions for the system $A \xrightarrow{k_1} B \underset{k_3}{\overset{k_2}{\rightleftarrows}} C$ are explored for characteristic features which are useful to the kineticist in determining the rate constants from fragmentary experimental data. It is found that B exhibits a maximum whenever $k_3 < k_1$. This maximum and the time at which it occurs are among the most useful features in determining the rate constants.

A critical examination of the pseudostationary state approximation for B as applied to this system is made, and a related approximation to C is introduced. The approximations are found to have a similar range of validity.

The time at which C is at an arbitrary percent of its equilibrium concentration is studied. Under certain conditions this time is essentially independent of one or more of the rate constants.

"An Expansion of $J_\nu(\nu x)$ in Powers of $(1/\nu)$" by C. F. Curtiss (supported by NASA) - Report No. WIS-TCI-7.   dated 17 December 1962

Abstract

Series expansions in powers of $(1/\nu)$ of the Bessel function, $J_\nu(\nu x)$, $J_\nu(\nu x)^2$, and the integral of the product of the square with an arbitrary function are developed. Each term in the expansion of $J_\nu(\sqrt{} x)$ is a sum of a finite number of derivatives of the delta function, $\delta(x - 1)$. Each term in the expansion of the square of the Bessel function is a sum of a finite number of derivatives of $g(x^2 - 1)$, where $g(x)$ is the discontinuous function defined by $g(x) = x^{-\frac{1}{2}}$ for $x \geq 0$ and $g(x) = 0$ for $x < 0$. Each term in the expansion of the integral is a finite number of integrals involving derivatives of the arbitrary function.

"A Study of One and Two Electron Central Force Problems Using the Hypervirial Theorem" by Sidney L. Gordon   dated 10 January 1963 (supported by NASA and Air Force)- Report No. WIS-TCI-8.

Abstract

The hypervirial theorem is used to develop expectation value relationships for one and two electron central force problems.

Ground state helium trial functions are scaled to identically satisfy a particular family of these relationships. It is shown that this procedure results in improved expectation values for positive powers of the radial coordinate.

"An Expansion of Binary Collision Phase Shifts in Powers of h"
by C. F. Curtiss   dated 16 January 1963
(supported by NSF) - Report No. WIS-TCI-9.

Abstract

The phase shifts in binary collisions are expressed as series in increasing powers of Plancks constant, h . The series begins with a term in h^{-1} and contains all odd powers. Recursion relations are developed which lead to an expression for an arbitrary term in the series. The results apply to an arbitrary interaction potential function, for which any odd number of classical turning points may arise.

"Truncated Reaction Operators and the Helium Problem" by William J. Meath, Kenneth M. Sando, S. Osvaldo Goscinski and Joseph O. Hirschfelder (supported by NASA, Air Force, and Bureau of Naval Weapons) - Rpt. No. WIS-TCI-10.
dated 25 February 1963

Abstract

The truncated reaction operator is used to obtain approximate solutions to the helium problem. Basis sets comprised of configurational interaction wave functions which have been constructed from products of uniformly scaled hydrogenic 1s and 2s functions are used. Approximate energies, wave functions and reaction operator matrix elements for the $(1s)^2$, $(1s)(2s)$ and $(2s)^2$ ^1S states are tabulated. The convergence of the method is discussed for specific examples with the aid of the Feenberg perturbation series.

"The Hypervirial Theorem for Collisions Between Electrons and Atoms"
by Michael B. McElroy and Joseph O. Hirschfelder   dated 8 March 1963
(supported by NASA and Air Force) - Report No. WIS-TCI-11.
Accepted for publication in Phys. Rev.

Abstract

The hypervirial theorem was first introduced for bound state systems and subsequently extended to one electron scattering problems. In this paper electron-atom collisions are considered and the appropriate form of

the hypervirial theorem is derived. Its relation to the original formulation is discussed. Application is made to the electron hydrogen problem. Both elastic and inelastic collisions are investigated.

"Comparison of the Hartree-Fock Orbital with the First Natural Spin Orbital for Two-Electron Systems" by George V. Nazaroff and Joseph O. Hirschfelder (supported by NASA and Air Force) -Rpt. #WIS-TCI-12. dated 25 March 1963 Scheduled to be published in 8/1/63 issue of J. Chem. Phys.

Abstract

A demonstration is given that for two-electron systems the Hartree-Fock and first natural spin orbitals are different functions. The method used is perturbation theory for which the zero-order problem is the Hartree-Fock approximation. A perturbation expansion through the second order is obtained for the first natural spin orbital. The two orbitals begin to differ in the second order and their energies in the fourth order. An equation for the second order part of the orbital difference function is derived. Estimates of the norms of the orbital difference functions are calculated for the ground states of the helium atom and the hydrogen molecule and are found to be small.

"Solutions For Complex Systems of Chemical Reaction Kinetics. Part III. A Reversible Unimolecular Reaction Followed by an Irreversible Unimolecular Reaction" by Dennis W. Kuba and Daniel D. Konowalow dated April 1963 (supported by Air Force) - Report No. ARL-(number not yet listed).

Abstract

This is the third in a series of reports in each of which a unimolecular chain reaction with an idealized type of chemical kinetics is carefully scrutinized. The integrated rate equations for the system $A \underset{k_4}{\overset{k_1}{\rightleftharpoons}} B \overset{k_2}{\longrightarrow} C$ are explored for characteristic features which are useful in the determination of rate constants. Only systems with the initial conditions $A = A_o$, $B = 0$ and $C = 0$ at $t = 0$ are considered.

Rate-determining processes for the overall reaction are found by treating a number of limiting cases in which one or more of the rate constants are small compared to others.

The reaction is defined to be complete when $C/A_o = 0.99$, and $t(0.99)$ is used as a reference time.

The steady state hypothesis is invoked to obtain approximate expressions for the concentration of B and C . The two approximations are found to have somewhat similar ranges of validity.

"The Integration of the First-Order Perturbed Wave Equation for Excited States of One Dimensional Systems" by W. Byers Brown and Joseph O. Hirschfelder (supported by NASA and Air Force) - Rpt. # WIS-TCI-13. dated 15 May 1963 Scheduled to be published in July issue of Proc. of Nat'l Acad. of Sci.

Abstract

The explicit solutions of the first-order perturbation equations for a one dimensional system can be obtained by quadratures provided that the zeroth-order wave function does not have any nodes. Methods of integrating the equations are developed for excited states where the zeroth-order wave function has nodes. One of these methods is suitable for obtaining numerical solutions.

"Resonance Method in Scattering Theory" by Egil A. Hylleraas (supported by NASA) - Report No. WIS-TCI-14. dated May 1963

Abstract

This article was originally meant to precede a second article, where now definitions and notations used here also are described in more detail. This part will here be cut down to a minimum.

The aim of the investigation is to replace the ordinary treatment of the scattering problem by an indirect one. This can be done by providing the scattering potential with an adjustable numerical factor which is used as an eigenvalue parameter of a discrete eigenvalue problem.

The term ₘresonance method" simply alludes to the structure of the formulae.

"On the Inversion of Eigenvalue Problems" by Egil A. Hylleraas (supported by NASA) - Report No. WIS-TCI-15. dated May 1963

"Determination of a Perturbing Potential From Its Scattering Phase Shift and Bound States Energy Levels" by Egil A. Hylleraas (supported by NASA)- Report No. WIS-TCI-16. dated May 1963

"Expansions of Integrals of Bessel Function of Large Order" by C. F. Curtiss   dated 27 May 1963 (supported by NASA and NSF) - Report No. WIS-TCI-17.

Abstract

Series expansions in powers of $1/\nu$ of integrals of the product of the Bessel function $J_\nu(\nu x)$, $\left[J_\nu(\nu x) \right]^2$, or $J_\nu(\nu x) J_{\nu+1}(\nu x)$ with an arbitrary function of a restricted class are developed.

"Hypervirial Functions and the Positive Powers of the Radial Coordinate
Operator in He and H⁻" by Sidney L. Gordon   dated 10 June 1963
(supported by NASA and Air Force) - Report No. WIS-TCI-18.

"Truncated Reaction Operators" by William J. Meath, Kenneth M. Sando,
S. Osvaldo Goscinski, and Joseph O. Hirschfelder   dated 18 June 1963
(supported by NASA, Air Force, and Bureau of Naval Weapons)- Rpt. # WIS-TCI-19.
Submitted for publication to J. Chem. Phys.

Abstract

The reaction operator formulation for the exact solution of the
Schrödinger equation is used with a truncated basis set to obtain approximate solutions. The relationship between this truncated reaction operator
formalism and the Rayleigh-Ritz variational method is emphasized and shown
explicitly. The truncated reaction operator and its matrix elements are
discussed in general; computed and discussed for a simple example, the
helium atom, using a three membered basis set. It is shown that the
reaction operator can be replaced by a function which we call the "effective"
perturbation. This function has very fundamental significance and may lend
itself to accurate empiricism. Expressions are given comparing the "effective"
perturbation with the perturbation and approximations to this function for
the helium atom are computed.

"Generalization of Laplace's Expansion to Arbitrary Powers and Functions of
the Distance Between Two Points" by R. A. Sack   dated 21 June 1963
(supported by NASA) - Report No. WIS-TCI-20.

Abstract

In analogy to Laplace's expansion, an arbitrary power r^n of the
distance r between two points, $(r_1, \vartheta_1, \varphi_1)$ and $(r_2, \vartheta_2, \varphi_2)$, is
expanded in terms of Legendre polynomials of $\cos \vartheta_{12}$. The coefficients
are homogeneous functions of r_1 and r_2 of degree n satisfying simple
differential equation; they are solved in terms of Gauss' hypergeometric
function of the variable $(r_</r_>)$. The transformation theory of hypergeometric functions is applied to describe the nature of the singularities
as r_1 tends to r_2 and of the analytic continuation of the functions past
these singularities. Expressions symmetric in r_1 and r_2 are obtained
by quadratic transformations; for $n = -1$, one of these has previously
been given by Fontana. Some 3-term recurrence relations between the radial
functions are established, and the expressions for the logarithm and the

inverse square of the distance are discussed in detail.

For arbitrary analytic functions $f(r)$ three analogous expansions are derived; the radial dependence involves spherical Bessel functions of $(r_< \partial / \partial r_>)$ or of related operators acting on $f(r_>)$, $f(r_1 + r_2)$ or $f\left[(r_1^2 + r_2^2)^{\frac{1}{2}}\right]$.

"Iteration-Variation Procedures for Quantum Mechanical Perturbations"
by Joseph O. Hirschfelder   dated 24 June 1963
(supported by NASA) - Report No. WIS-TCI-21.
Submitted for publication to ~~Proc. of Nat'l Acad of Sci.~~ Journal of Chemical Physics

Abstract

The Dalgarno-Lewis procedure is used for obtaining explicit solutions to the perturbation equations. Three basic ideas are exploited: 1). By using the wave function through the first order as the zeroeth order wave function in a new perturbation calculation, we obtain an iteration procedure that converges with surprising rapidity. After n iterations, the energy is given accurately up to terms of the order of the 2^{n+1} power of a perturbation parameter. 2). By varying the proportions of the zeroeth and first order function in the wave function through the first order, we obtain somewhat better energies and still maintain the ability to iterate. And 3). For degenerate and almost-degenerate energy levels, the wave functions through the first order and the energies through the third order are obtained by solving a finite ordered secular equation. This procedure is much simpler and less apt to fail than the usual techniques.

"Elastic Scattering of Atoms and Molecules in the Thermal Energy Range"
by Richard B. Bernstein   dated 28 June 1963
(supported by Bernstein's own funds) - Report No. WIS-TCI-22.

Abstract

The goal of research on elastic scattering of atomic (or molecular) beams is the elucidation of the interaction potential $V(r)$. The present discussion is confined to thermal energy collisions (< 1 ev), sensitive primarily to the attractive part of the potential. Studies of the velocity dependence of the differential and total elastic scattering cross sections have yielded information as follows: (1) The functional form of the long-range attraction: $V \sim -C/r^6$, from differential cross sections $I(\theta)$, at low angles: $I(\theta) \propto \theta^{-7/3}$. (2) The attractive potential constant C,

from total cross sections: $Q \propto (C/v)^{2/5}$. (3) The depth of the potential well ϵ , from the rainbow effect in $I(\theta)$: $\theta_r = f(\tfrac{1}{2}\mu v^2/\epsilon)$. (4) The equilibrium separation r_m , from de Broglie interference producing undulations in $I(\theta)$. (5) The product ϵr_m , from extrema in $Q(v)$, and thus r_m (from absolute Q's). (6) Observation of $\underline{m}$ maxima in plots of $vQ^{5/2}$ vs. v^{-1} (termed elastic impact spectra) implies the existence of at least $\underline{m}$ bound states (discrete vibrational levels of zero angular momentum for the composite system).

Additional Publications During Fiscal Year 1962-63

"Power Series Solutions for Energy Eigenvalues" by Don Secrest, K. Cashion and J. O. Hirschfelder, J. Chem. Phys., 37, 830 (1962).
(supported by AEC)

"Natural Expansions of Exact Wave Functions I. Method" by E. R. Davidson J. Chem. Phys., 37, 577 (1962).
(supported by AEC and Air Force)

"Molecular Collisions IV. Nearly Spherical Rigid Body Approximation" by George Gioumousis and C. F. Curtiss, J. Math. Phys., 3, 1059 (1962).
(supported by NSF)

"Direct-Product Representation of Wave Functions" by E. R. Davidson and Leon L. Jones, J. Chem. Phys., 37, 1616 (1962).
(supported by Bureau of Naval Weapons)

"Correlation Splitting in the Hydrogen Molecule" by E. R. Davidson and Leon L. Jones, J. Chem. Phys., 37, 1918 (1962).
(supported by Bureau of Naval Weapons)

"Equation of State for Binary Fluid Mixtures" by Charles E. Hecht J. Chem. Phys., 38, 1008 (1963).
(supported by Bureau of Naval Weapons)

"Some Remarks on the Theory of Flame Propagation" by J. O. Hirschfelder, published in a book entitled Ninth Combustion Symposium (published by Academic Press).

"On the Non-Orthogonality of Generalized Momentum Eigenfunctions in Quantum Mechanics" by P. D. Robinson, J. Math. Phys., 4, 348 (1963).
(supported by AEC)

"Generalized Momentum Operators in Quantum Mechanics" by P. D. Robinson and J. O. Hirschfelder, J. Math. Phys., 4, 338 (1963).
(supported by AEC)

"Applied Mathematics as Used in Theoretical Chemistry" by J. O. Hirschfelder, scheduled to be published in Proc. of Symposia in Applied Mathematics, Vol. 15.

"The Classical Hypervirial Relations" by J. O. Hirschfelder to be published in the Zeitschrift für Physikalische Chemie, special issue dedicated to Professor Wilhelm Jost (1963).
(supported by U.S. Army Research Office (Durham))